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ANODE FILM LAYER FOR GALVANIC CELLS
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This invention relates to permeable separating media for primary galvanic cells, and more particularly for the so-called dry cells. It relates more particularly to anode film layers comprising such separating media and to methods for their production.

The common form of dry cell comprises a metal anode, a cathode conductor element and an immediately disposed cathode depolarizer mix which is moistened with an appropriate electrolyte. Separating media are required to be interposed between the anode and the depolarizer mix to prevent internal short circuits of the electrodes, but it is also necessary in the interests of economical and satisfactory operation that the separator media be ionically permeable to permit passage of electrolyte and soluble products of decomposition of the anode.

A generally accepted requirement for such separator media is that they comprise on one surface a material which when disposed in contact with the anode, and when wetted with electrolyte, will firmly adhere in moist, sticky relation to the anode. This may be termed the "anode film" layer or portion of the separator medium. The anode film portion being at least partially soluble or capable of migration in the electrolyte, an electrolyte-insoluble film portion or zone is required to protect the relatively soluble anode film portion or zone from migration from the anode. This electrolyte-insoluble portion may be termed the "barrier film" portion or zone. It is essential that each of these portions or zones be ionically permeable to allow passage of electrolyte and electrolyte-soluble anode decomposition products through them. A further requirement of the barrier layer is that it does not allow transfer of the anode film components to the cathode.

It is an object of the present invention to provide an anode film particularly adapted for employment in dry cells. It is a further object to provide a method for satisfactorily bonding such anode film portion to a barrier film portion to provide a unitary separator film. It is a still further object to provide a means facilitating application of an anode film layer to a metal anode.

The anode layer of the invention is prepared by dissolving a predetermined quantity of a binder consisting of a polymerized ester of an unsaturated alcohol and an acid in a low molecular weight organic solvent. Next, a quantity of an electrolyte-soluble, water-swellaable colloid is suspended in the solution. The binder here holds the colloid particles in place on the anode or on the separator support. The suspension can be spread, poured, or painted onto a support sheet of plastic, paper or on the anode metal itself.

Suitable readily hydrolyzed polymerized esters of unsaturated alcohols and acids include the polyvinyl, polyacrylic, polymethacrylic and polymaleic esters of low molecular weight acids, such as formic, acetic, propionic acids as well as copolymers of the foregoing, such as those of polyvinyl acetate and polyallyl acetate. A particularly useful and desirable member of the group of esters of polymerized unsaturated alcohols is polyvinyl acetate. The amount of binder used may be varied widely, depending on many factors, including the molecular weight of the selected resin, the solubility in the selected solvent, and the colloid concentration desired for the intended application. Generally, the binder will con-

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stitute from about 1 to about 10 percent by weight of the colloid-resin-solvent mixture.

Examples of low molecular weight organic solvents are acetone, ethyl ether, ethyl alcohol, chloral, chloroform, cyclopentane, heptane, hexane, cyclohexane, pentane, dioxane and generally low molecular weight alcohols, ketones and ethers which are compatible with the selected hydrolyzable polymerized ester.

Generally, the solvent can be chosen solely on the basis of its solvent power for the resin selected and for the insolubility of the colloid therein. Economic, solvent recovery and toxicity factors will also influence solvent selection.

The colloids found operative in this invention must be compatible with cell electrolytes, must not be readily oxidized by the cell cathode, must not be readily hydrolyzed by cell electrolyte, must not be swollen by organic solvents, and must swell in cell electrolyte. Suitable colloids or colloid-forming materials include methyl cellulose ether, carboxymethyl methyl cellulose, sodium carboxymethyl cellulose, polyvinyl alcohol, hydroxy propyl methyl cellulose, the calcium salts of the copolymer of maleic anhydride and vinyl acetate and equivalent materials as well as various gums. As employed herein, "gums" refers to a class of colloidal substances, glutinous when moist, but hardening on drying, exuded by or extracted from plants. Suitable gums and gum-like materials include guar gum, locust bean gum, gum karaya, gum tragacanth, low methoxy pectin and gelatin. Mixtures of the foregoing are also very attractive for given applications as one ingredient can be used to provide the viscosity desired for handling, while the second component provides the necessary adhesive characteristics. Depending upon the use requirements, and on the specific colloid, the amount thereof will range from about 5 to about 20 percent by weight of the colloid-resin-solvent mixture.

One of the particular advantages of the present invention is that it enables the casting of suitable anode films on an electrolyte-insoluble barrier film, a metal anode or other support from high solids content suspensions.

As an example of the method of forming the anode film layer of the present invention, particles of water-soluble methyl cellulose are suspended in an acetone solution of polyvinyl acetate and applied to the barrier film, a metal anode or a film-forming support. The acetone is then substantially evaporated, and the remaining film comprising water-soluble methyl cellulose ether and polyvinyl acetate results. Surprisingly, the presence of polyvinyl acetate in the anode film layer does not alter or substantially affect the ability of the anode film to maintain adherence to the metal anode, nor does it interfere with or affect the operation of a galvanic cell in which it is incorporated. In the anode film of this embodiment, the polyvinyl acetate serves as a compatible binder for water-soluble methyl cellulose particles or fibers, and the resulting anode film, which is a mixture of water-soluble methyl cellulose and polyvinyl acetate, is well adapted to production of dry cells having long and satisfactory shelf life and service life.

Various grades and types of methyl cellulose may be employed according to this invention. Satisfactory water-soluble methyl cellulose should have a methoxy content of at least 27 percent. Various viscosity grades of methyl cellulose ether may be employed, but in general viscosity grades of 1000 to 4000 cps. are preferred.

Various types and grades of polyvinyl acetate may be employed. However, those types are preferred which give a relatively tack-free film upon evaporation of solvents. In general, a polyvinyl acetate having a softening point of 80° C. or above is preferred, although polyvinyl ace-

tate having a somewhat lower softening point may also be used.

It will be understood that upon volatilization of the acetone or of the other lower aliphatic oxygenated organic compounds, they may be recovered for re-use. Various solvent recovery methods will occur to one skilled in the art.

EXAMPLE 1

To 50 ml. of acetone there is added 3 grams of polyvinyl acetate with rapid agitation. Agitation is continued until the polyvinyl acetate is dissolved. Then, 9.52 grams of 4000 cps. water-soluble methyl cellulose ether is slowly stirred in. One ml. of water was added to facilitate suspension of the methyl cellulose. The solution was then poured onto a barrier film consisting of cast alkali-soluble methyl cellulose which had a 10.2 percent methoxy content, and which was supported on a horizontal glass plate. The acetone rapidly evaporated from the suspension and a unitary film resulted having a barrier film portion consisting of alkali-soluble methyl cellulose and an anode film portion comprising water-soluble methyl cellulose and polyvinyl acetate.

EXAMPLE 2

Three grams of polyvinyl acetate were dissolved in 300 ml. of acetone, and in this solution were suspended 9.52 grams of No. 1350 "Hydrophil" (karaya gum). This suspension was evenly poured onto high wet strength alpha cellulose paper (S-17), which had been previously dampened and taped onto a 300 sq. in. glass plate. When solvent evaporation had occurred, a dry smooth composite film resulted. These are only two of the methods by which the anode film may be applied. Others include brush-type applications, dough-roll coating applications, and perhaps many more not herein mentioned. If a smoother suspension of the colloid-resin mixture is desired, it may be ball milled for any desired length of time.

Similarly, a representative group of separators was prepared using quantities of materials listed in Table I below.

Table I

COMPOSITION OF ANODE FILM LAYERS APPLIED TO VARIOUS SUPPORT LAYERS

Example No.	Resin and quantity	Solvent and volume
1-----	3 g. polyvinyl acetate-----	150 ml. carbon tetrachloride.
2-----	3 g. polyvinyl formal-----	50 ml. ethylene dichloride.
3-----	3 g. polyvinyl acetate-----	300 ml. acetone.
4-----	3 g. Hecosee "S" (cellulose acetate sorbate).	200 ml. ethyl acetate.
5-----	3 g. polyvinyl acetate-----	300 ml. acetone.
6-----	do-----	Do.
7-----	do-----	Do.
8a-----	5.7 g. polyvinyl acetate-----	81 ml. acetone.
8b-----	6.0 g. polyvinyl acetate-----	70 ml. acetone.

Example No.	Colloid and quantity of anode layer	Support layer or barrier
1-----	9.52 g. carboxy-methyl methyl cellulose.	Alkali-soluble methyl cellulose.
2-----	9.52 g. water-soluble sodium carboxy methyl cellulose.	Sodium cellulose sulfate.
3-----	9.52 g. Gum karaya-----	S-17 paper.
4-----	9.52 g. hydroxy propyl methyl cellulose.	Do.
5-----	9.52 g. calcium salt of copolymer of maleic anhydride and vinyl acetate.	Do.
6-----	do-----	Do.
7-----	9.52 g. locust bean gum-----	Do.
8a-----	3 g. 4,000 cps., water soluble methyl cellulose.	Zinc.
8b-----	do-----	Do.

NOTE.—The quantities given in Examples 1 to 6 above were combined and used to coat an approximate 300 sq. in. area.

A small sample of each of these separator preparations was placed in Leclanché cell electrolyte consisting of 23 percent zinc chloride, 28 percent ammonium chloride, and 49 percent water to determine the length of time required for complete disintegration of the resin-bonded colloid layer. These data are shown in Table II. Ordinarily, if 4000 cps. water soluble film is placed in this electrolyte, it will disintegrate within 15 minutes. It may be noted that a somewhat longer period is required in this film where hydrolysis or deterioration of the resin binder must occur before the colloidal material may be released. It should be noted, too, that the products of resin breakdown themselves may aid in the promotion of a sticky, anode contact.

Table II

COMPOSITION AND SOLUBILITY OF SUPPORTED ANODE FILM LAYERS IN LECLANCHÉ CELL ELECTROLYTE

Example No.	Disintegration time in dry cell electrolyte
1-----	1 day.
2-----	Do.
3-----	Do.
4-----	Do.
5-----	Do.
6-----	After 2 days film had not disintegrated, but was very sticky and a gelatinous mass.
7-----	
8-----	
	1 day.

The separators identified may use a flexible supporting sheet on which the resin-colloid-solvent anode film portion can be spread. In addition to the materials above indicated, the support, in an alkaline cell, may consist of a woven or non-woven sheet of plastic fibers, rayon or nylon. Laminated support layers also may be used. Thus, a paper base layer may be first coated with a film-forming resin and dried, and then coated with the resin-bonded colloid layer.

Separators made as above were placed in a dry cell consisting of pre-amalgamated zinc cans with the resin-colloid film intermediate the depolarizer mix and the anode film. To follow the rate at which hydrolysis or degradation of the resin occurred, voltage and amperage readings on the fresh cells were made periodically. These readings are shown in Table III.

Table III

RAPIDITY OF HYDROLYSIS IN EXPERIMENTAL LECLANCHÉ CELLS

Example No.	Voltage and amperage readings					
	Approx. 5 hrs. old		3 Days		2 Weeks	
	V.	A.	V.	A.	V.	A.
1-----	1.60	6.6	1.60	6.1	1.35	3.6
2-----	1.45	5.8	1.35	4.8	1.55	5.6
3-----	1.55	6.8	1.45	5.6		
4-----	1.65	6.9	1.60	6.3	1.43	4.0
5-----	1.65	6.2	1.65	6.0		
6-----	1.65	6.3	1.63	5.9		
7-----	0.4	0.4	0.4	0+		
8-----	1.62	6.3	1.55	6.0	1.38	4.2
9-----	1.45	5.9	1.25	3.2		
10-----	1.65	7.2	1.65	6.5	1.63	6.2
11-----	1.65	6.7	1.47	5.4	1.54	5.4
12-----	1.64	7.2	1.55	6.2		

Table IV

SHELF AND SERVICE SUMMARY ON FIRST EXPERIMENTAL CELLS MADE WITH PVAc, 4000 CPS. METHOCCEL, ALKALI SOLUBLE ANODE FILM LAYER

Service test	4-ohm, 4-Min. LIF—Minutes to 1.1, 0.9, 0.8 v.					
Experimental.....	(329) (576) (624)					
Control.....	(343) (540) (611)					
21° C. Shelf	2 Weeks		6 Mos.		12 Mos.	
	V.	A.	V.	A.	V.	A.
	Experimental.....	1.54	3.9	1.60	4.4	1.60
Control.....	1.64	6.1	1.60	5.1	1.59	4.8

Service Test	4-ohm, 4-Min. LIF—Minutes to 1.1, 0.9, 0.8 v.				2.25-ohm LIF—Minutes to 0.65 v.			
Experimental.....	(496) (858) (1,117)				634			
Control.....	(528) (1,013) (1,136)				593			
21° C. Shelf	24 Mos.		36 Mos.		48 Mos.		60 Mos.	
	V.	A.	V.	A.	V.	A.	V.	A.
	Experimental.....	1.59	3.9	1.56	4.2	1.57	4.6	1.53
Control.....	1.59	3.7	1.57	3.5	No more cells available			

Although their initial voltage and amperage values were not quite as high as the control cells, they did have extremely good voltage and current maintenance even after five years storage. The cells used for control were film-lined laboratory assembled cells. They contained 4000 cps., water-soluble Methocel, anode film, with mercuric chloride amalgamating agent, used in combination with alkali-soluble methyl cellulose barrier film.

In another embodiment of the invention, a suspension was made up by the formulae presented in Table I—Examples 8a and 8b. The suspension was painted directly onto the inside of the zinc can and then dusted with a little additional 4000 cps., water-soluble methyl cellulose and dried. The barrier layer, in the form of an aqueous solution of sodium cellulose sulfate, and bobbin were then added. The service date of these cells as compared with the factory product cells are presented in Table V. These data compare favorably, and visual inspection of the discharged cells showed that a very good contact existed between the anode film and the zinc can, thus proving that the anode film can be successfully applied to a zinc anode surface.

Table V

COMPARISON OF INITIAL SERVICE DATE OF EXPERIMENTAL "FILM ON ANODE" LINED WITH FACTORY PRODUCT PASTE-LINED C SIZE, CELLS

Identification	Separator	
	Anode	Barrier
No. 35 Experimental.....	PVAc + Methocel.....	Na Cellulose SO ₄
Factory Product.....		
Identification	4-ohm Continuous—Min. to 0.75 v.	4-ohm LIF—Min. to 0.9 v.
	No. 35 Experimental.....	153
Factory Product.....	120	208

A major advantage of the present invention is that the anode film thereof can be tailor-made from a great variety of resins and colloids so as to be useful in many cell systems employing diverse anodic materials including zinc and magnesium as well as various electrolytes.

The invention has other advantages. Not only are

cells of excellent quality produced thereby, but the lining of the anodes can be carried out in an economical way well adapted to automatic machines. Moreover, the invention permits a conforming lining to be applied to anode surfaces of any shape.

This application is a continuation-in-part of application Serial No. 549,161, filed November 25, 1955, and now abandoned.

What is claimed is:

10 1. A method for producing an anode film portion of a separator medium galvanic cells, which method comprises suspending at least one water-swellaable organic colloid in a volatile low molecular weight organic compound containing a readily hydrolyzed polymerized ester of an unsaturated alcohol, applying said suspension to a support and removing said organic compound by volatilization.

2. A method for producing an anode film portion of a separator medium for galvanic cells, which method comprises suspending an electrolyte-soluble, water-swellaable organic colloid in a volatile low molecular weight organic compound containing a readily hydrolyzed polymerized ester of an unsaturated acid, applying said suspension to a support and removing said organic compound by volatilization.

3. A method for producing an anode film portion of a separator medium for galvanic cells, which comprises suspending an electrolyte-soluble, water-swellaable organic colloid in a volatile low molecular weight oxygenated aliphatic organic compound containing a readily hydrolyzed polymerized ester of an unsaturated alcohol, applying said suspension to a support and removing said low molecular weight oxygenated aliphatic organic compound by volatilization.

4. The method of claim 3, wherein the low molecular weight oxygenated aliphatic organic compound is acetone.

5. The method of claim 3, wherein the low molecular weight oxygenated aliphatic organic compound is ethyl ether.

6. The method of claim 3, wherein the low molecular weight oxygenated aliphatic organic compound is ethyl alcohol.

7. The method of claim 3, wherein the readily hydrolyzed polymerized ester of an unsaturated alcohol is polyvinyl acetate.

8. A method for producing an anode film portion of a separator medium for galvanic cells, which comprises suspending an electrolyte-soluble, water-swellaable organic colloid in a volatile low molecular weight oxygenated aliphatic organic compound containing a readily hydrolyzed polymerized ester of an unsaturated alcohol, applying said suspension to a metal anode for a galvanic cell, and removing said oxygenated aliphatic organic compound from said suspension by volatilization.

9. The method of claim 8, wherein the anode metal is a metal selected from the group consisting of zinc, magnesium and alloys thereof.

10. A method for producing a separator medium for galvanic cells, which comprises suspending an electrolyte-soluble, water-swellaable organic colloid in a volatile low molecular weight oxygenated aliphatic organic compound containing a readily hydrolyzed polymerized ester of an unsaturated alcohol, applying the resulting suspension to a film adapted to serve as a barrier film portion for galvanic cells, and removing said oxygenated aliphatic organic compound from said suspension by volatilization.

11. A separator medium for galvanic cells comprising a barrier film portion having bound thereto an anode film portion of an unsaturated ester and at least one water-soluble organic colloid selected from the group consisting of carboxymethyl methyl cellulose, sodium carboxymethyl cellulose, hydroxymethyl cellulose, hydroxypropyl methyl cellulose, calcium salts of the copolymer of maleic anhydride and vinyl acetate, gum karaya, guar gum, locust bean gum, polyvinyl alcohol, pectin and mixtures thereof.

12. A method for producing an anode film portion of a separator medium for galvanic cells, which method comprises suspending water-soluble methyl cellulose ether in a volatile low molecular weight organic compound containing a readily hydrolyzed polymerized ester of an unsaturated alcohol, applying said suspension to a support and removing said organic compound by volatilization.

13. A method for producing an anode film portion of a separator medium for galvanic cells, which method comprises suspending water-soluble methyl cellulose ether in a volatile low molecular weight organic compound containing a readily hydrolyzed polymerized ester of an unsaturated acid, applying the resulting suspension to a support and removing said organic compound by volatilization.

14. A method for producing an anode film portion of a separator medium for galvanic cells, which comprises suspending at least one water-soluble methyl cellulose ether in a volatile low molecular weight oxygenated aliphatic organic compound containing a readily hydrolyzed polymerized ester of an unsaturated alcohol, applying the resulting suspension to a support and removing said low molecular weight oxygenated aliphatic organic compound by volatilization.

15. The method of claim 14, wherein the low molecular weight oxygenated aliphatic organic compound is acetone.

16. An anode film portion for galvanic cells comprising a readily hydrolyzed polymerized ester of an unsaturated alcohol and a water-soluble methyl cellulose ether.

17. An anode film portion for galvanic cells comprising a water-soluble methyl cellulose ether in admixture with a polyvinyl carboxylate.

18. A separator medium for galvanic cells comprising a barrier film portion having in securely bound relation thereto, an anode film portion comprising water-soluble methyl cellulose ether in admixture with a polyvinyl carboxylate.

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